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<b>(21) International Application Number:</b> PCT/GB93/00164 <b>(22) International Filing Date:</b> 26 January 1993 (26.01.93) <b>(71) Applicant (for all designated States except US):</b> ZENECA LIMITED [GB/GB]; Imperial Chemical House, Millbank, London SW1P 3JF (GB). <b>(72) Inventor; and</b> <b>(75) Inventor/Applicant (for US only):</b> DE KONING, Gerardus, Johannes, Maria [NL/NL]; Hoogstraat 86-B, NL-5615 PS Eindhoven (NL). <b>(74) Agents:</b> MANNION, Sally, Kim et al.; ICI Group Patents Services Dept., P.O. Box 6, Bessemer Road, Welwyn Garden City, Hertfordshire AL7 1HD (GB).		<b>(81) Designated States:</b> CA, JP, US.  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> POLY[(R)-3-HYDROXYBUTYRATE] BASED POLYESTER  <b>(57) Abstract</b>  A polyester consisting essentially of poly[(R)-3-hydroxybutyrate] units in which ageing has occurred, characterised in that (i) the polyester is restored to its original non-aged properties by a heat treatment, and (ii) subsequent ageing of the polyester is retarded as indicated by substantial stability of at least one measurement indicative of ageing. The invention also includes a process of de-ageing aged polyester, and shaped polyester articles subjected to the de-ageing process.		

## POLY[(R)-3-HYDROXYBUTYRATE] BASED POLYESTER

THIS INVENTION relates to polyester and shaped polyester articles in particular to polyester and such articles restored to their original non-aged properties after ageing has taken place and a process of de-ageing such polyester and articles.

Whereas the polyester poly[(R)-3-hydroxybutyrate] (PHB) when freshly moulded shows ductile behaviour, subsequent ageing seriously embrittles it and hampers its applicability. Within several weeks of storage at room temperature, the tensile modulus doubles, and the elongation at break drops below 10%. A mild de-ageing treatment by the employment of heat up to 70°C results in a slight and temporary improvement in mechanical properties.

It has now been found that such ageing can be reversed by a defined heat treatment and the so-treated polyester and articles are less subject to subsequent ageing.

According to the present invention there is provided a polyester consisting essentially of poly[(R)-3-hydroxybutyrate] units in which ageing has occurred, characterised in that (i) the polyester is restored to its original non-aged properties by a heat treatment, and (ii) subsequent ageing of the polyester is retarded as indicated by substantial stability of at least one measurement indicative of ageing.

According to a further aspect of the invention there is provided a shaped article at least partly made of polyester consisting essentially of poly[(R)-3-hydroxybutyrate] units in which ageing has occurred, characterised in that (i) the shaped article is restored to its original non-aged properties by heating, and (ii) subsequent ageing of the shaped article is retarded as indicated by substantial stability of at least one measurement indicative of ageing.

"At least partly made" means having structural components made of PHB to such an extent that ageing of the PHB components ages the whole article. Thus for example, PHB may be

absence of plasticiser. It consists of repetitive units of formula I:



where m is 3 or 4 and n is 2m or 2m-2. Typically C<sub>m</sub>H<sub>n</sub>

5 contains 2 carbon atoms in the polymer chain and a C<sub>1</sub> or C<sub>2</sub> side chain on the carbon next to oxygen in the chain. Particular polyesters contain at least 99 mol% of m=3 units, the remainder being m = 4 units or fractional percentages of units having higher values of m. The molecular weight Mw of  
10 the PHB is for example from 50000 to 2 x 10<sup>6</sup>, especially over 100000.

The PHB can be a product of fermentation, especially of a microbiological process in which a microorganism lays down PHB during growth or is caused to do so by cultivation in  
15 starvation of one or more nutrients necessary for cell multiplication. The microorganisms may be wild or mutated or may have the necessary genetic material introduced into it. Alternatively the necessary genetic material may be harboured by an eukaryote, to effect the microbiological process.

20 Examples of suitable microbiological processes are the following:

for Formula I material with m = 3 or m = partly 3, partly 4 :

EP-A-69497 (Alcaligenes eutrophus)

for Formula I materials with m = 3

25 US 410533 (A. eutrophus)

EP-A-144017 (A. latus);

The PHB can be extracted from the fermentation product cells by means of an organic solvent, or the cellular protein material may be decomposed leaving microscopic granules of PHB.

30 Alternately, the PHB can be a product of synthetic chemistry (Bloembergen, S. and Holden, D. A., Macromolecules. 1989, 22, p1656-1663).

The properties of the polyester or article of the present invention can be assessed using the following measurements :

inert gas or in vacuo, or in water or a fluid which does not interfere with the integrity of the polyester, or in a mould. Heat transfer can be by conduction, radiation, convection or resistive heating.

5 In the accompanying drawings:

Figure 1 shows stress-strain curves at ambient conditions days, (b) treated as in (a) and subsequently heated for 10 h at 100°C, (c) treated as in (b) and stored for another 120 days.

10 Example 1

Comparison of stress strain behaviour of aged samples and samples de-aged according to the present invention

PHB homopolymer powder ("BIOPOL" from ICI) having Mw 539000, Mw/Mn 3.5 was mixed with 1.0% of boron nitride nucleating agent in a Hobart (RTM) mixer for about 10 min. The mixture was fed to a Betol 2520 (RTM) 25 mm screw extruder operated at maximum 180°C temperature with a screw speed of 100 rpm. The 4 mm strand so produced was crystallised at 60°C in a water bath and granulated. The granules were dried at 40°C for 20 h and injection-moulded into specimen 2 x 5 x 12 mm using a Boy 15S (RTM) machine at a maximum barrel temperature 180°C, injection time 15 sec, screw speed 220 rpm, injection pressure 5MPa, mould temperature 60°C, cooling time 15 sec. The specimens were allowed to age for 150 days at ambient temperature. Then the specimens were subjected to the following treatments :

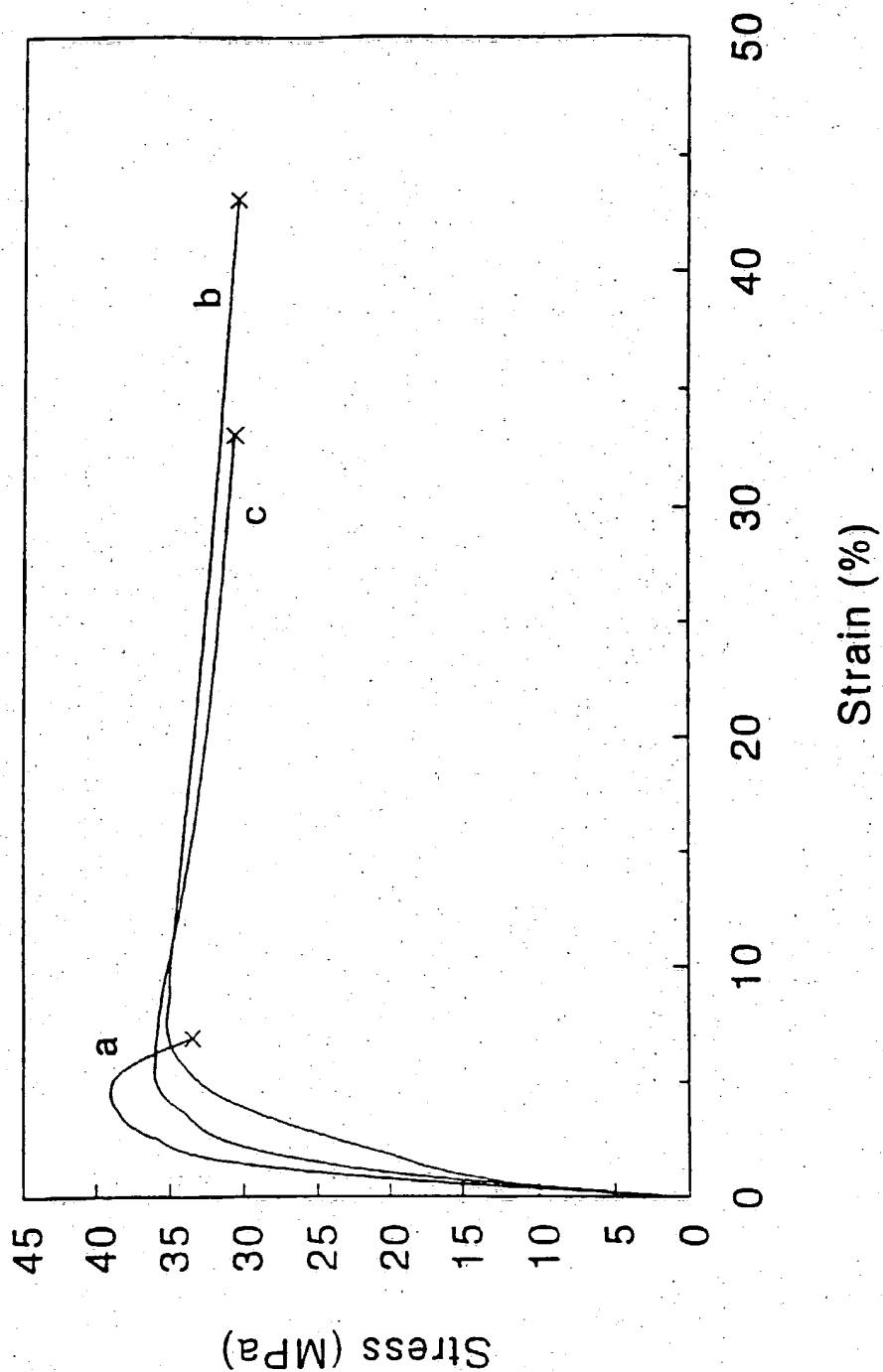
- (a) no further treatment
- (b) heated for 10 h at 100°C
- (c) treated as in (b) and stored for a further 120 days at ambient temperature.

30 The three specimens were examined for stress-strain behaviour using an Instron (RTM) 1122 tensile testing machine fitted with a Nene data analysis system. A clamp separation of 50 mm and a crosshead speed of 20 mm.min<sup>-1</sup> were used. The injection moulded specimens were dumbbell-shaped according to

## CLAIMS FOR PCT APPLICATION

- 1 A polyester consisting essentially of poly[(R)-3-hydroxybutyrate] units in which ageing has occurred, characterised in that (i) the polyester is restored to its original non-aged properties by a heat treatment, and (ii) subsequent ageing of the polyester is retarded as indicated by substantial stability of at least one measurement indicative of ageing.
- 2 A polyester according to claim 1 wherein the temperature of the treatment is from 90°C to 150°C.
- 3 A polyester according to claim 1 or 2 wherein the period of heat treatment is from 5 seconds to 20 hours.
- 4 A polyester according any of claims 1 to 3 in which the poly[(R)-3-hydroxybutyrate] (PHB) is a product of a fermentation process in which a microorganism lays down PHB during growth or is caused to do so by cultivation in starvation of one or more nutrients necessary for cell multiplication.
- 5 A process of de-aging an aged polyester consisting essentially of poly[(R)-3-hydroxybutyrate] units which comprises heating at a temperature whereby (i) the polyester is restored to its original non-aged properties, and (ii) subsequent ageing of the polyester is retarded as indicated by substantial stability of at least one measurement indicative of ageing.
- 6 A process according to claim 5 wherein the temperature is in the range from 90°C to 150°C.
- 7 A process according to claim 5 or 6 wherein the polyester is heated for 5 seconds to 20 hours.
- 8 A process according to any of claims 5 to 7 in which the poly[(R)-3-hydroxybutyrate] (PHB) is a product of a fermentation process in which a microorganism lays down PHB during growth or is caused to do so by cultivation in starvation of one or more nutrients necessary for cell

FIGURE 1



III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	<p>CHEMICAL ABSTRACTS, vol. 110, no. 24, 12 June 1989, Columbus, Ohio, US; abstract no. 213897z, M. SCANDOLA; ET AL 'The physical aging of bacterial poly(D-.beta.-hydroxybutyrate)' &amp; Makromol. Chem., Rapid Commun., 1989, 10(2), 47-50 (Eng) see abstract</p> <p>-----</p>	